

ICMGP 2024
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In Situ Remediation of Mercury in Groundwater

Geochemical Characterization and Modeling Are Keys to Success

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Former Chlor-Alkali Plant in NE United States

- Source area (former mercury cell building) cut off by bentonite slurry barrier wall
- Portion of groundwater Hg plume outside barrier wall discharges to nearby wetland



Groundwater Mercury Plume

- In situ chemical fixation (ISCF) by injection of sulfide to precipitate HgS determined to be most appropriate remedy

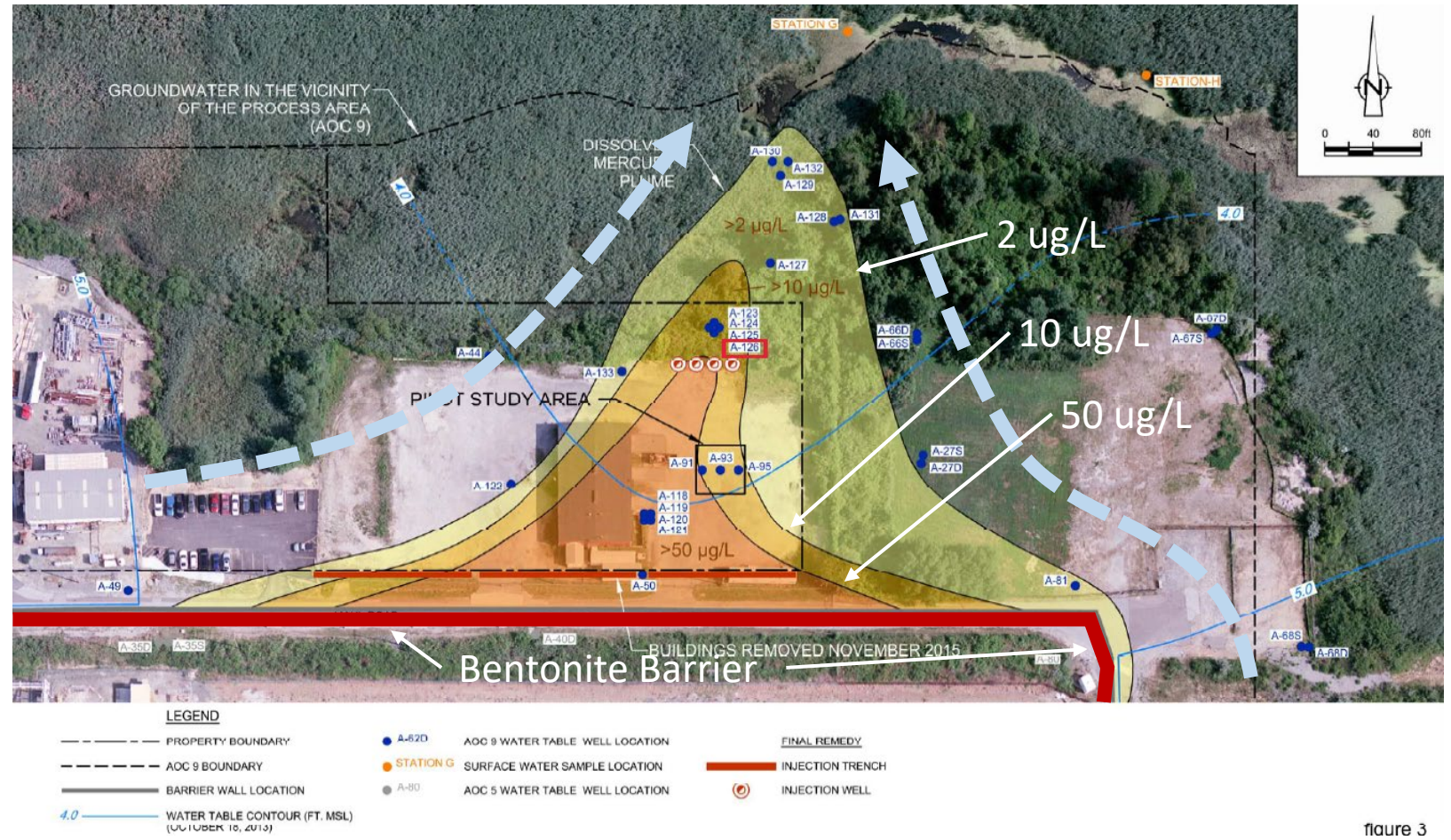
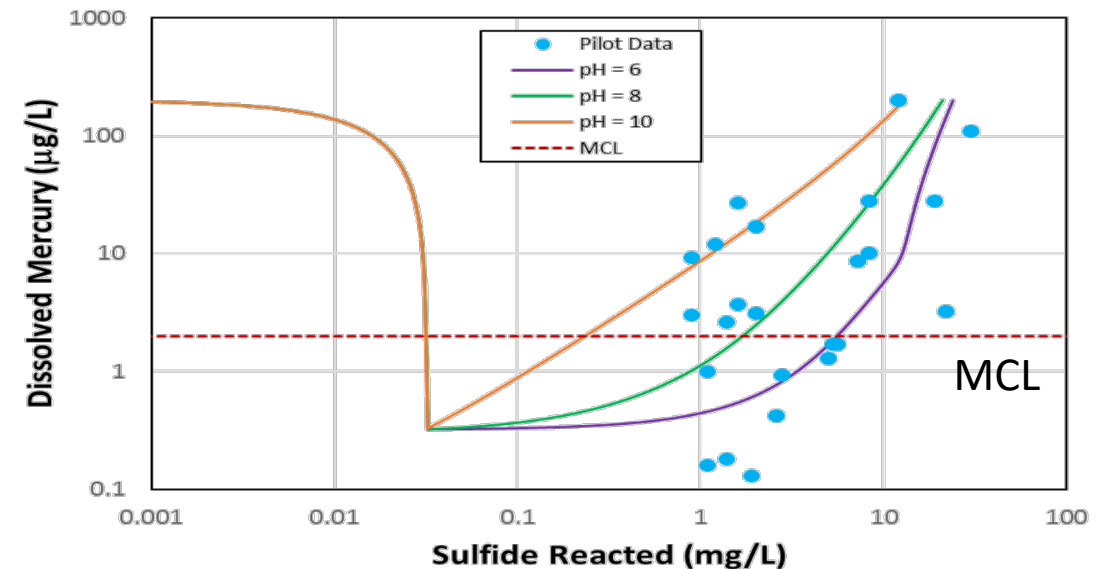
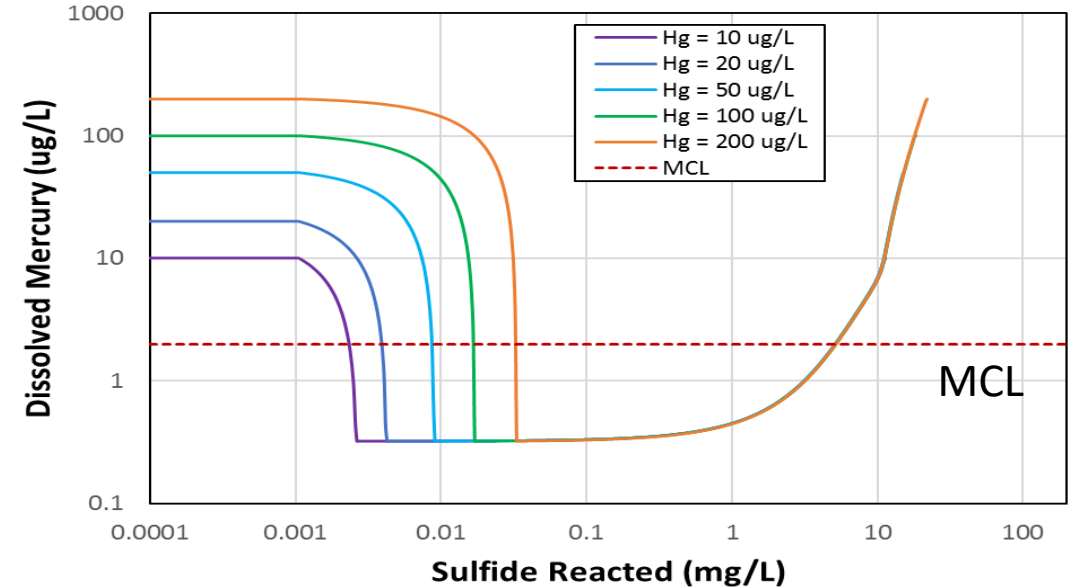


figure 3

ISCF Operating Windows



- Delivery of sufficient sulfide dose is a key challenge
- Target dose needs to account for:
 - Dissolved Hg
 - Sulfide-reactive Hg in aquifer matrix
 - pH, and
 - Sulfide demand from other components in groundwater and aquifer matrix
- Overdosing can result in Hg mobilization due to formation of Hg-sulfide complexes



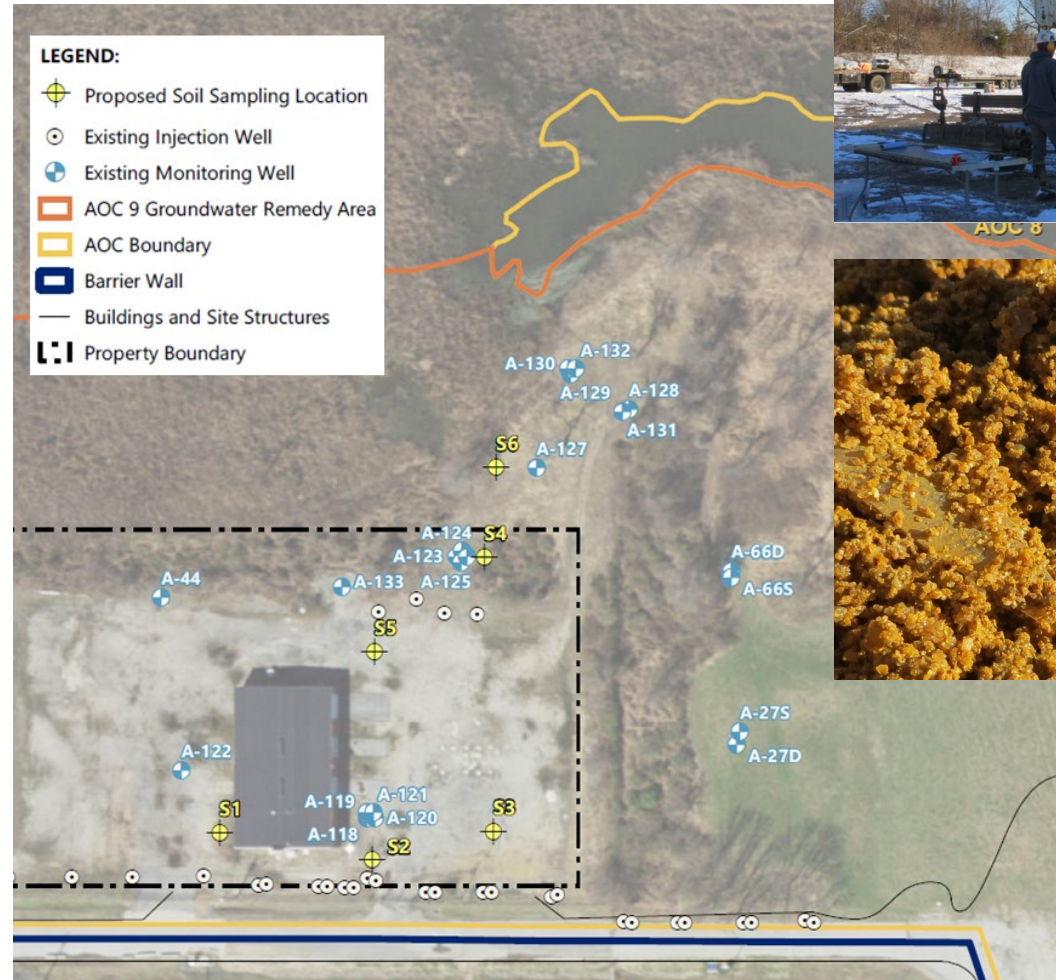
Accounting for Reagent Demand

- Target [Hg] and non-target [O₂, Fe(III), Mn(IV), Fe(II)] components that react with and consume sulfide
- Impact on reagent dose based on stoichiometric relations and groundwater and aquifer matrix characterization

Reactant	Reaction	Stoichiometric Demand ¹
Mercury	$\text{Hg}^{2+} + \text{HS}^- \rightarrow \text{HgS}_{(s)} + \text{H}^+$	1:1
Dissolved Oxygen	$\text{HS}^- + \frac{1}{2}\text{O}_2 + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{S}^0$	2:1
	$\text{HS}^- + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{S}_2\text{O}_3^{2-}$	1:1
	$\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$	1:2
Manganese(IV) oxides	$\text{HS}^- + \text{Mn}^{\text{IV}}\text{O}_{2(s)} + 3\text{H}^+ \rightarrow \text{S}^0 + \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1:1
	$\text{S}^0 + 3\text{Mn}^{\text{IV}}\text{O}_{2(s)} + 4\text{H}^+ \rightarrow \text{SO}_4^{2-} + 3\text{Mn}^{2+} + 2\text{H}_2\text{O}$	1:3
Iron(III) oxides	$\text{HS}^- + 2\text{Fe}^{\text{III}}\text{OOH}_{(s)} + 5\text{H}^+ \rightarrow 2\text{Fe}^{2+} + \text{S}^0 + 4\text{H}_2\text{O}$	1:2
	$\text{HS}^- + 8\text{Fe}^{\text{III}}\text{OOH}_{(s)} + 15\text{H}^+ \rightarrow 8\text{Fe}^{2+} + \text{SO}_4^{2-} + 12\text{H}_2\text{O}$	1:8
Iron(II)	$\text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS}_{(s)} + \text{H}^+$	1:1
	$\text{HS}^- + \text{Fe}^{2+} + \text{S}^0 \rightarrow \text{FeS}_{2(s)} + \text{H}^+$	1:2

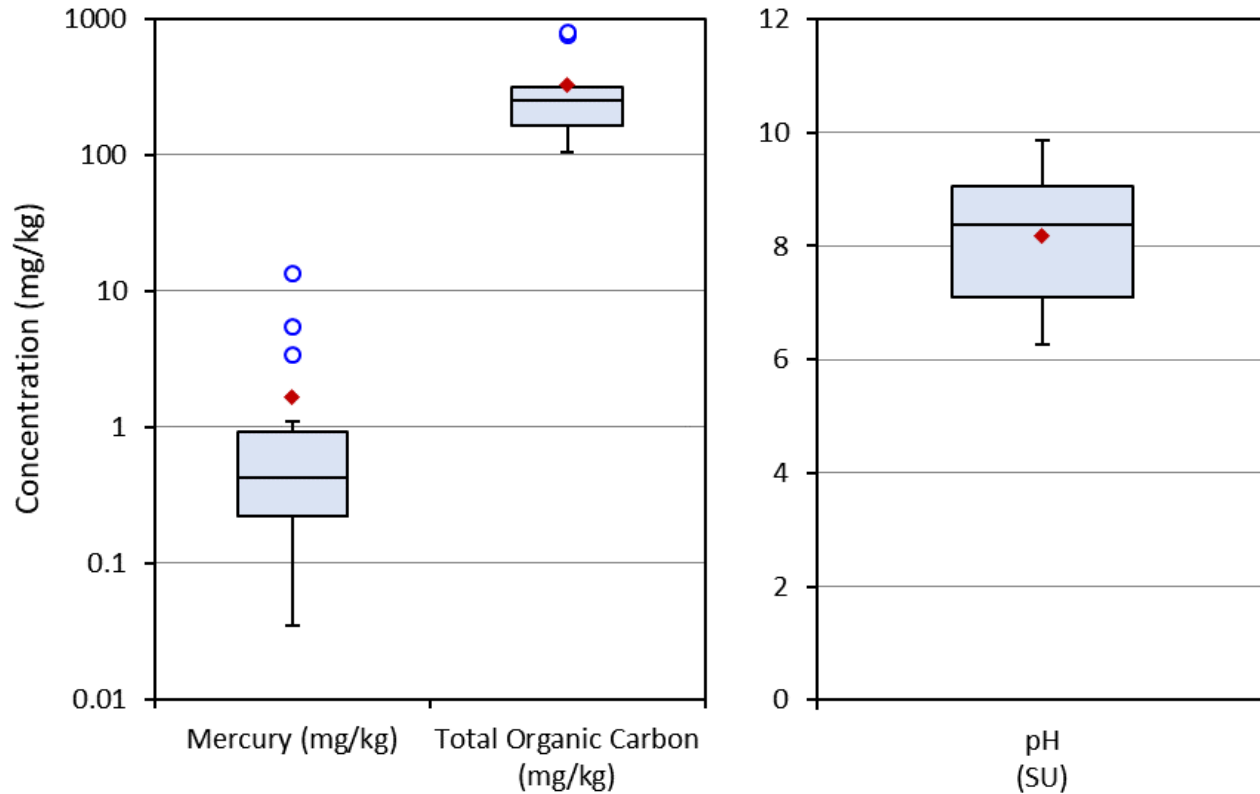
Reagent Demand Characterization

- Bulk Chemistry
 - Mercury
 - Sulfide
 - TOC
 - Iron
 - pH
- Mineralogy (XRD)
- Reactive Iron and Manganese
 - Mild Acid Extractable Iron
 - Extractable Iron Oxides
 - Extractable Manganese Oxides

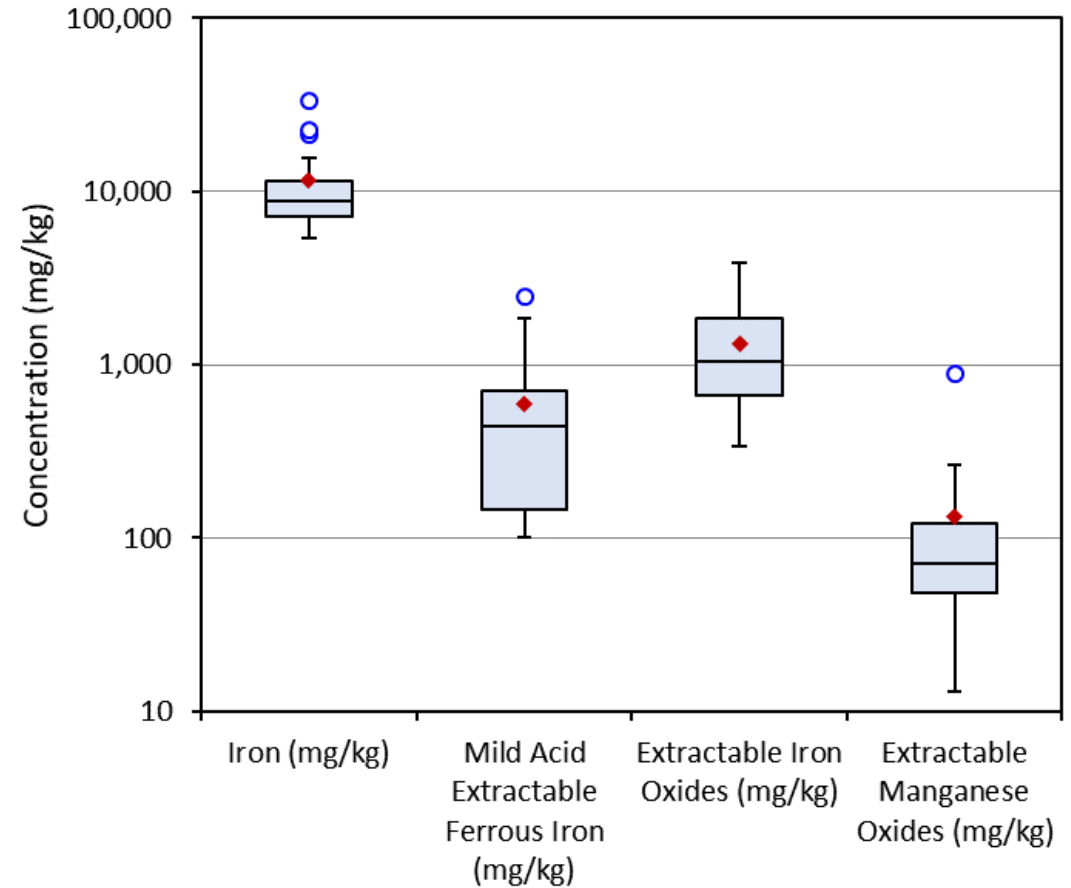


Aquifer Matrix Characterization

Bulk Chemistry



Reactive Iron and Manganese



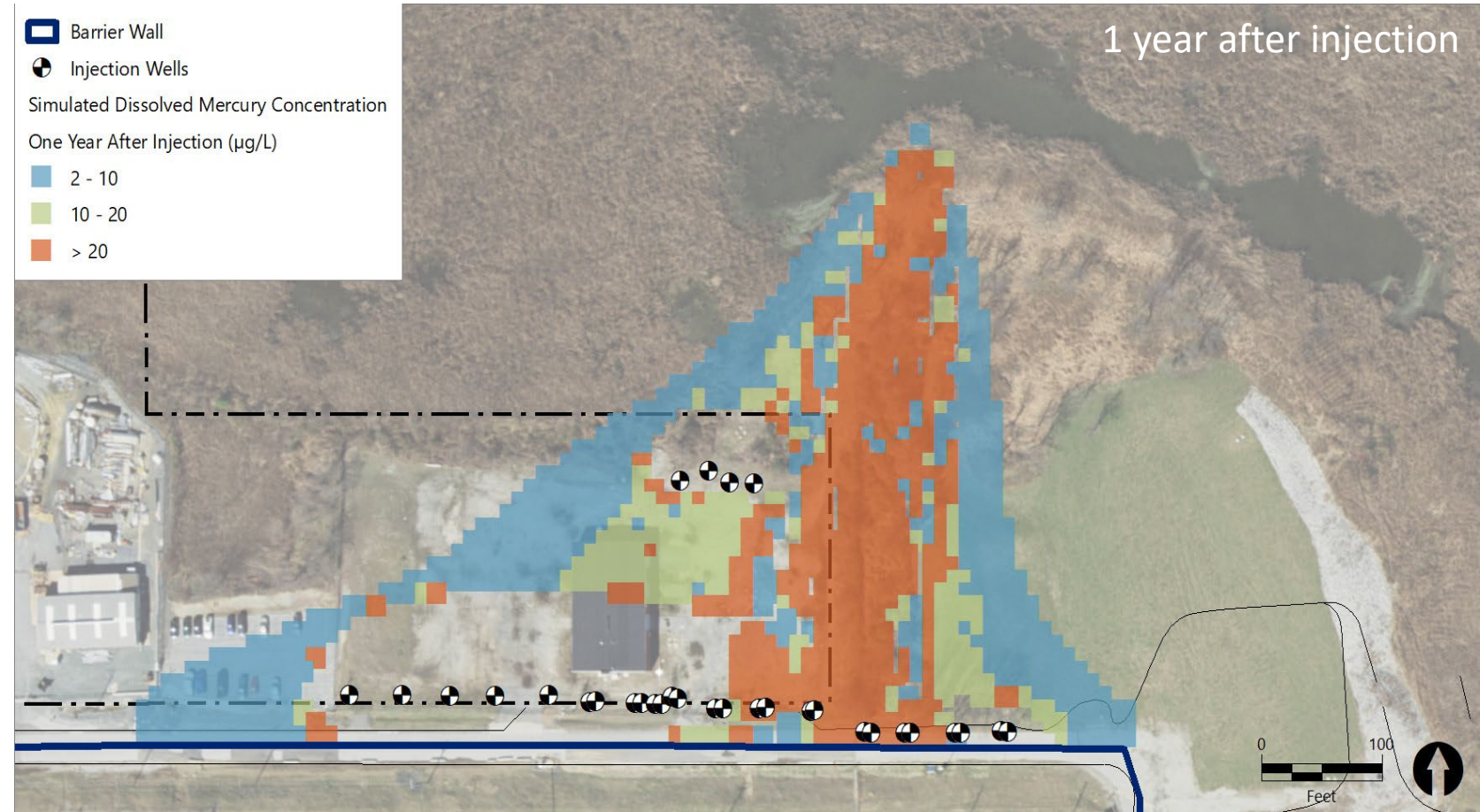
- 0-2 wt% iron oxides (goethite, magnetite)
- Sulfide <4 mg/kg

Injection Design

- Reactive transport model
 - Quantitatively account for groundwater flow and reagent demand
 - Evaluate reagent delivery approaches
 - Number and location of injection wells
- Develop injection parameters
 - Reagent dose (sodium sulfide concentration and injection volumes)
 - Predict plume evolution and treatment timeframe
 - Set expectations and support performance monitoring plan

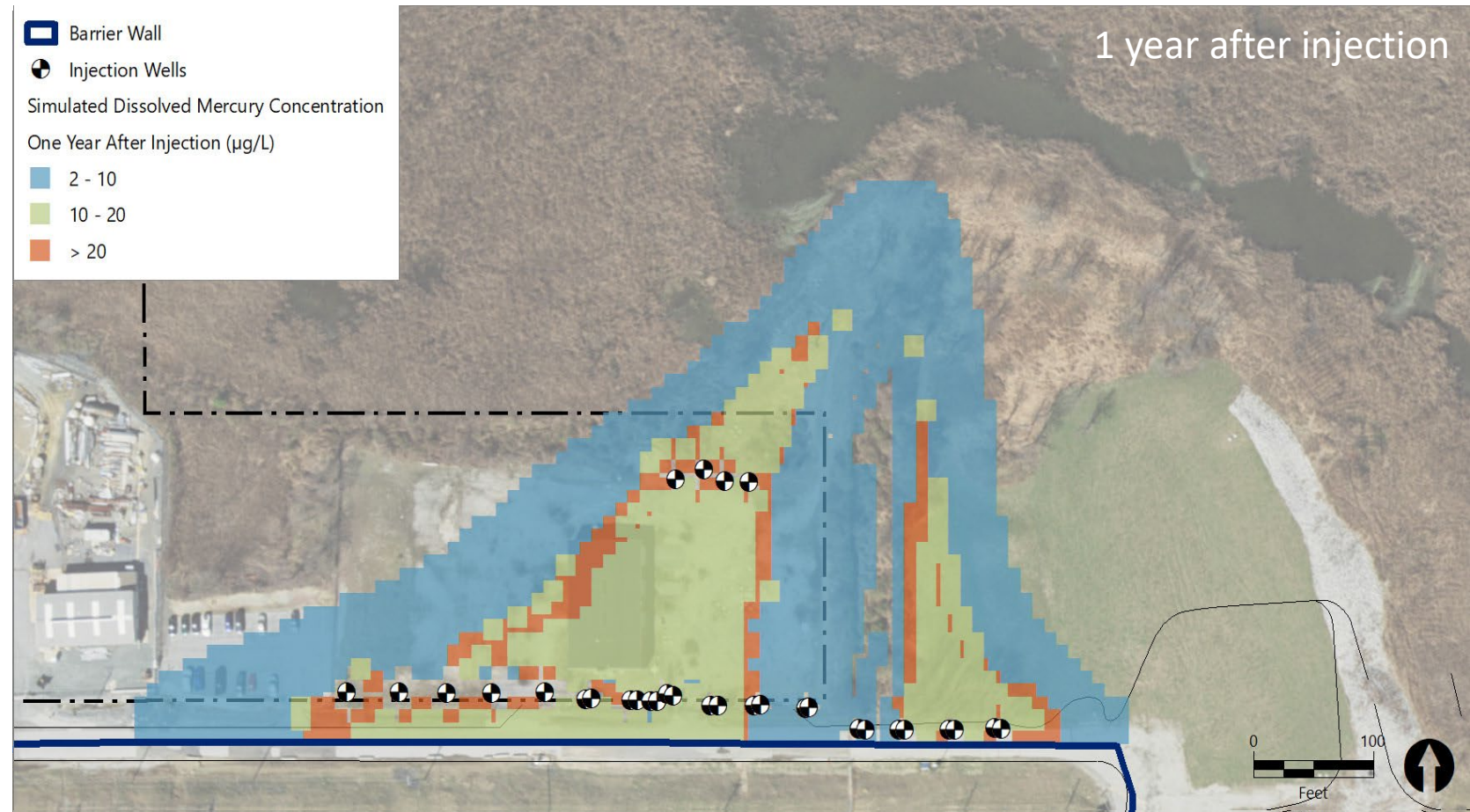
Injection Design Modeling

- Single injection of full sulfide dose
- Model predicts significant Hg mobilization from aquifer matrix
- HgS precipitation limited



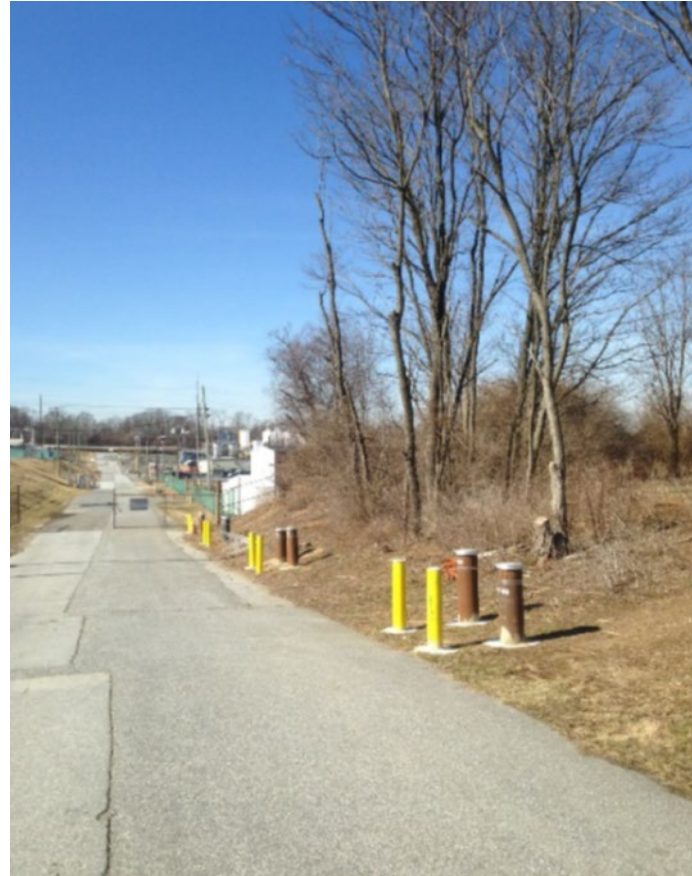
Injection Design Modeling

- Injection of partial sulfide dose (25%)
- Better control of Hg mobilization
- HgS precipitation more widely and uniformly distributed
- Allows for focused additional treatment of hot spots

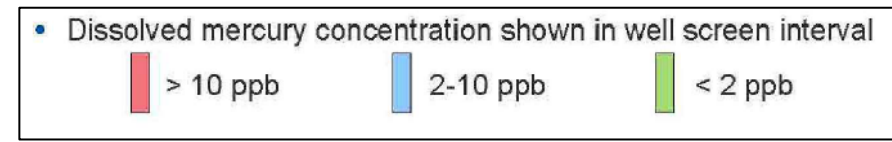
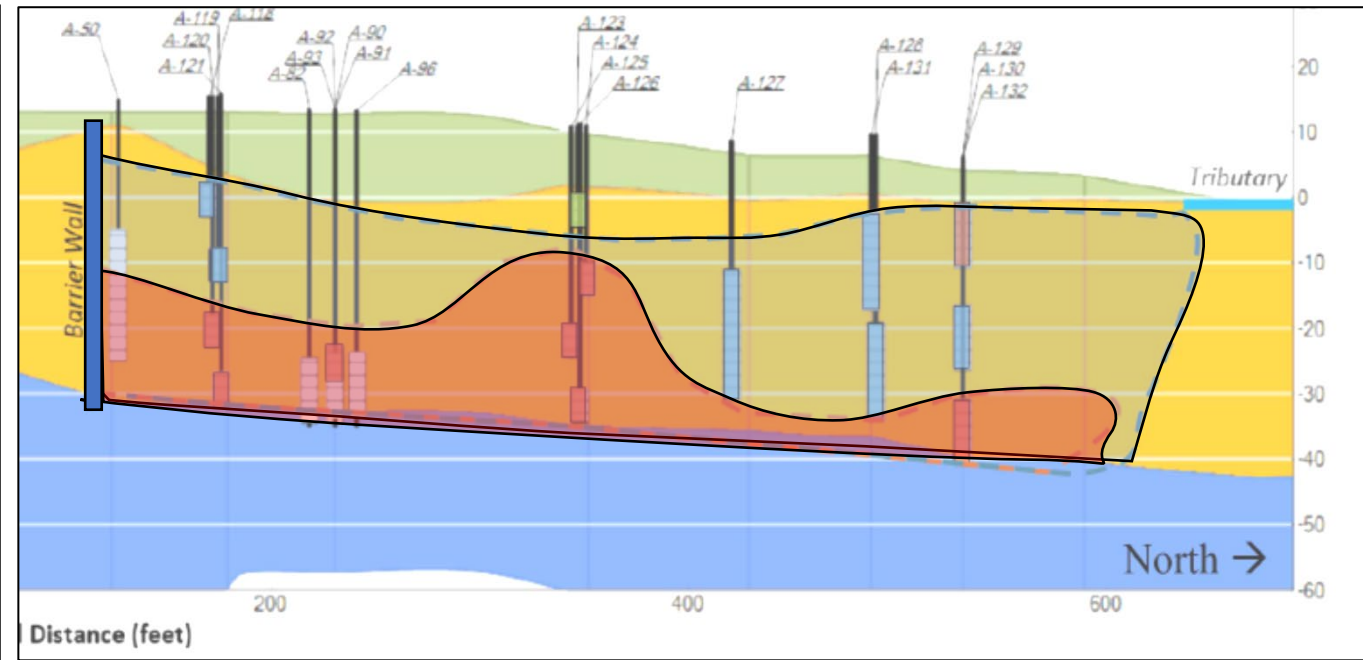
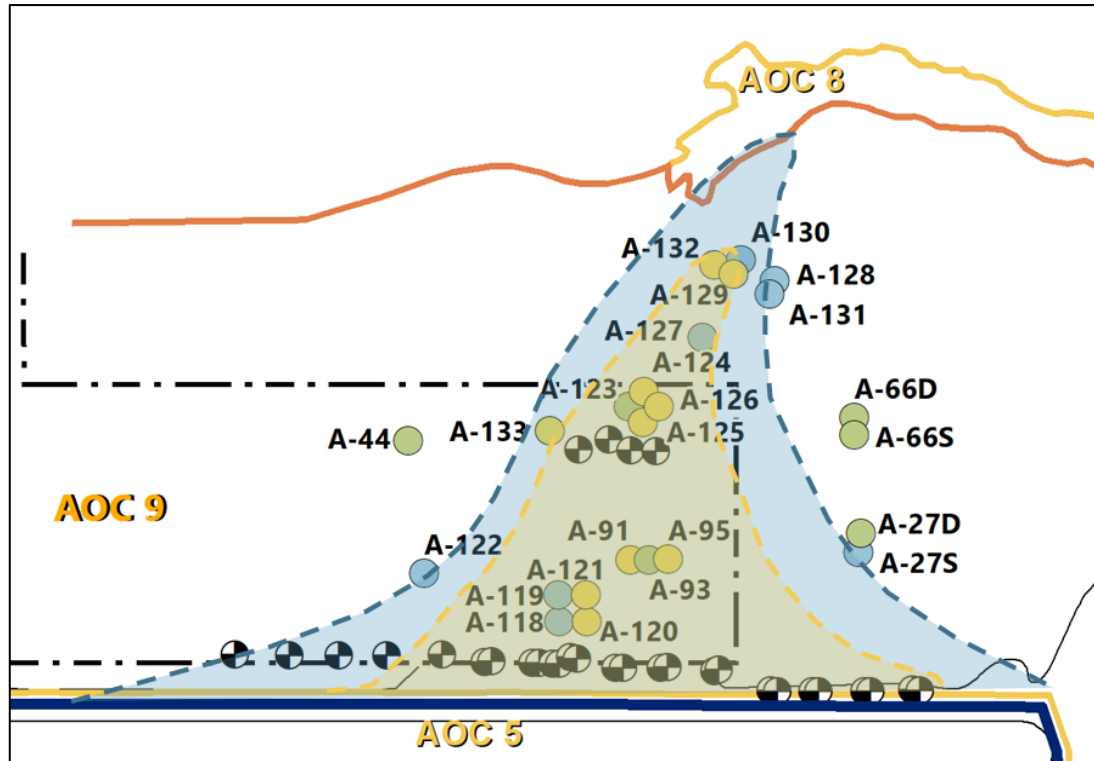


Injection Performed in 2019

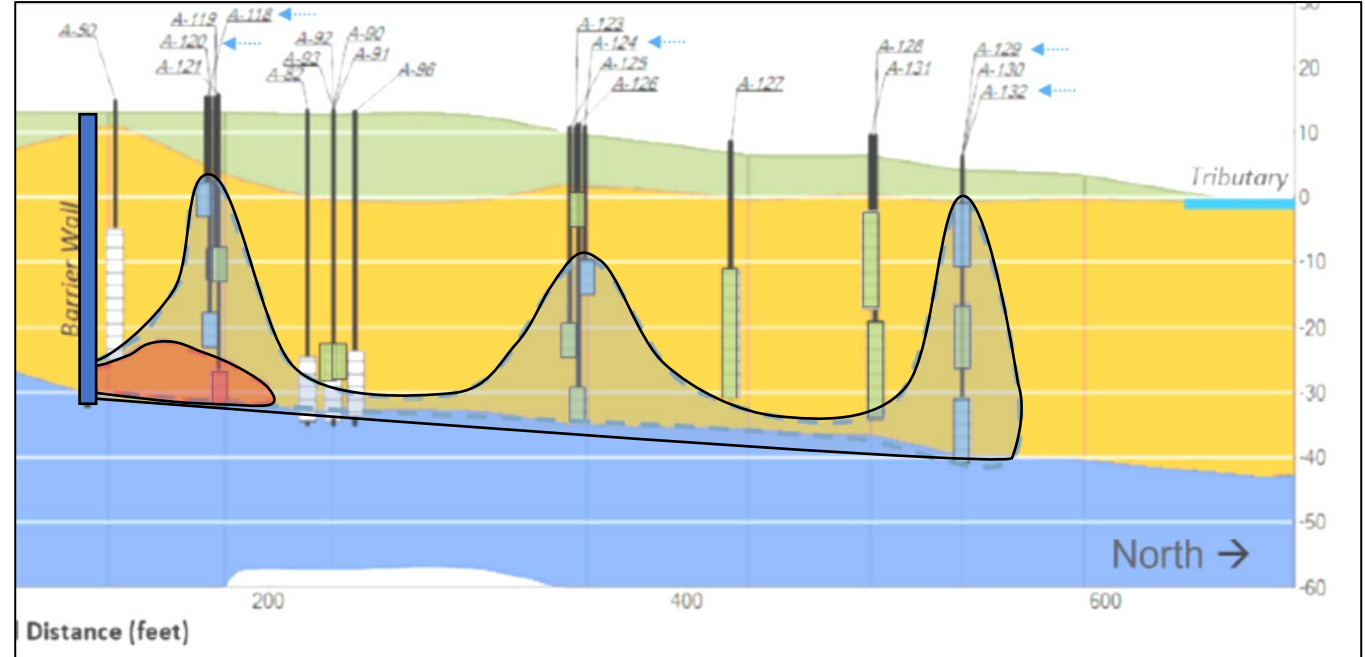
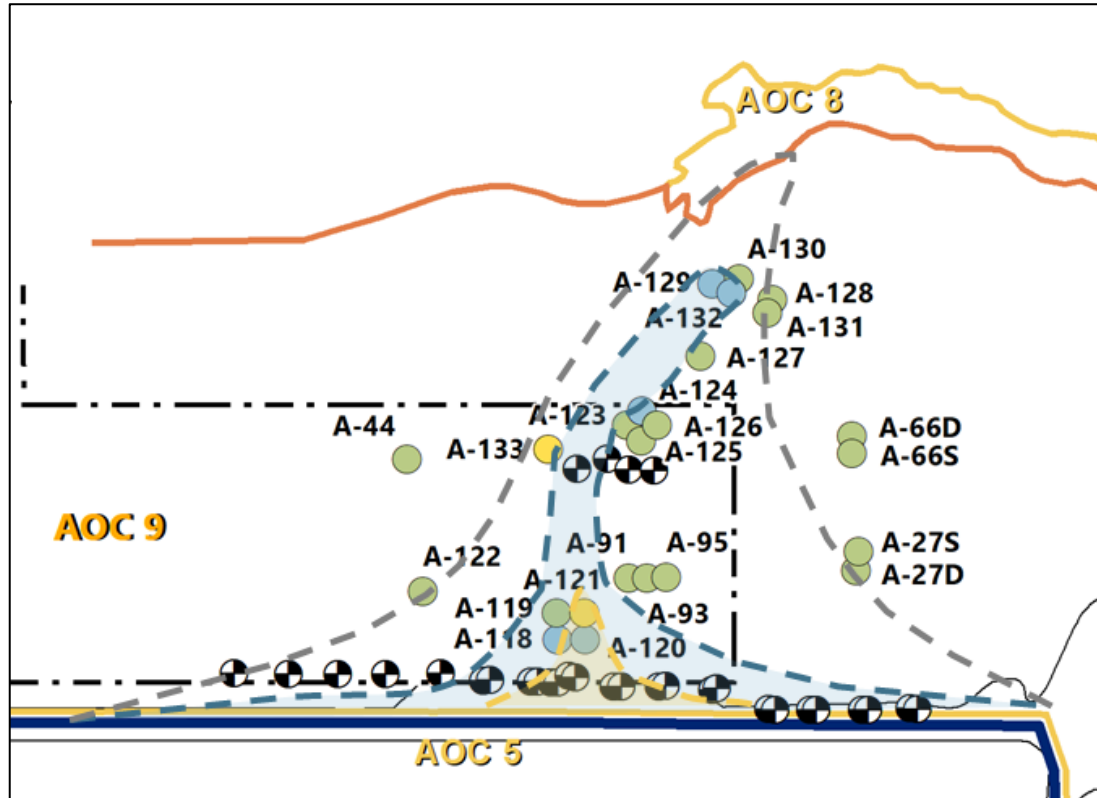
- 32 injection wells
 - 2 lines of wells
 - 2 depth intervals
- Injection solution:
0.15 M Na₂S
- Total volume of
~2×10⁶ L injected

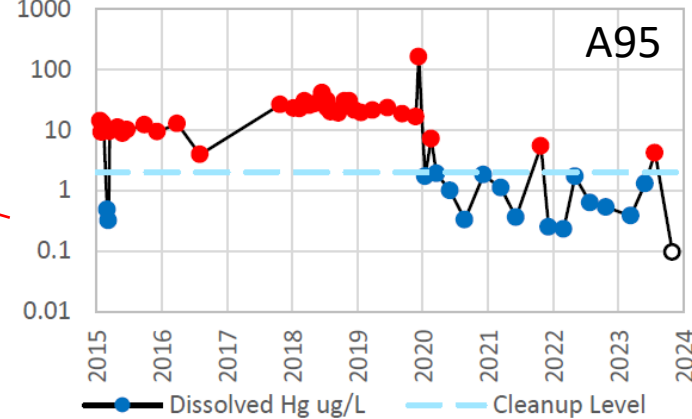
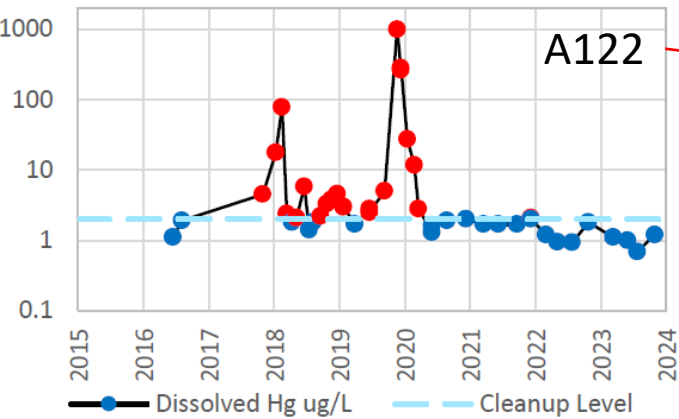
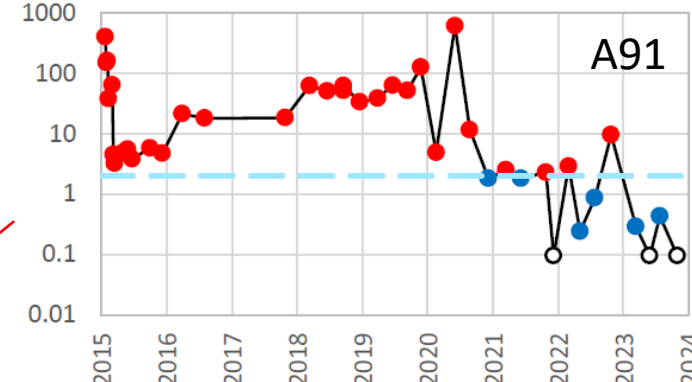
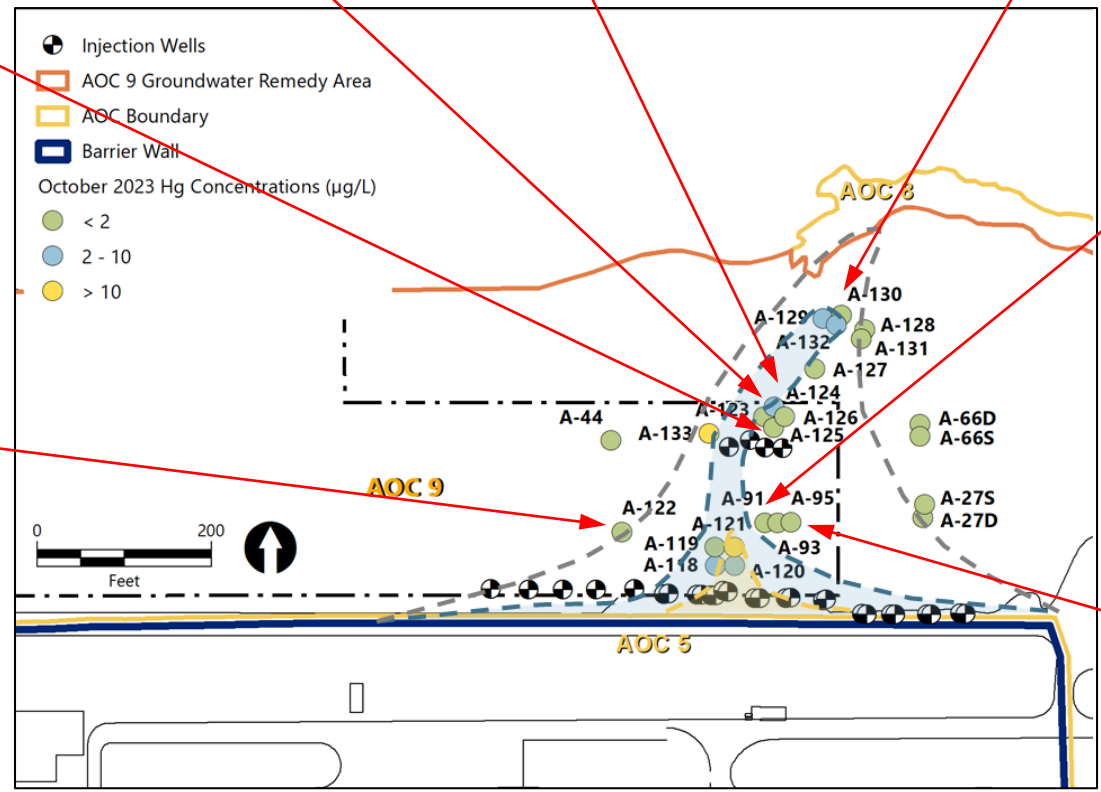
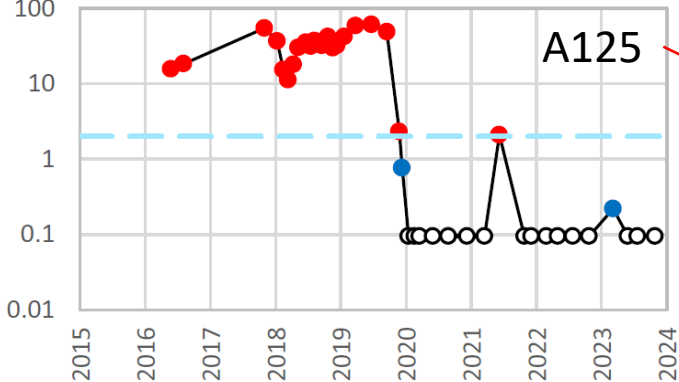
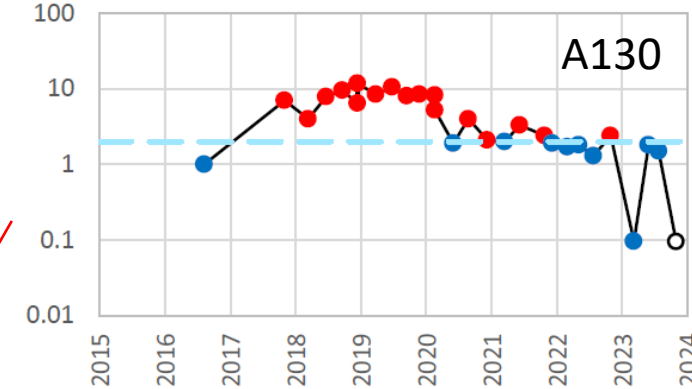
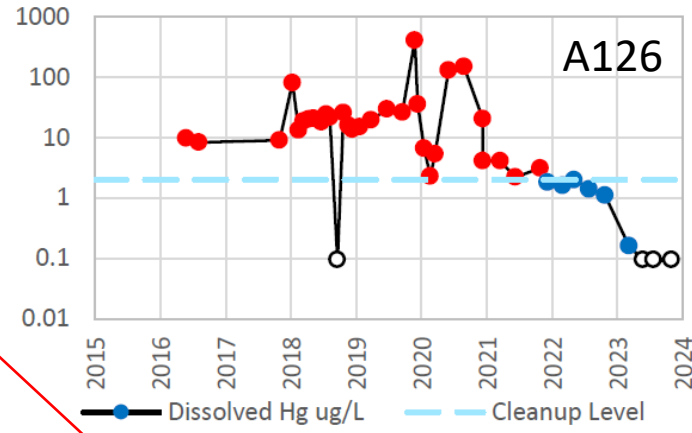
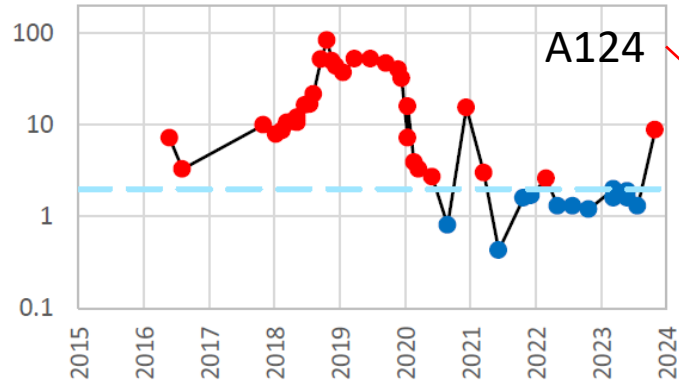


Hg Plume Prior to Injection (2019)



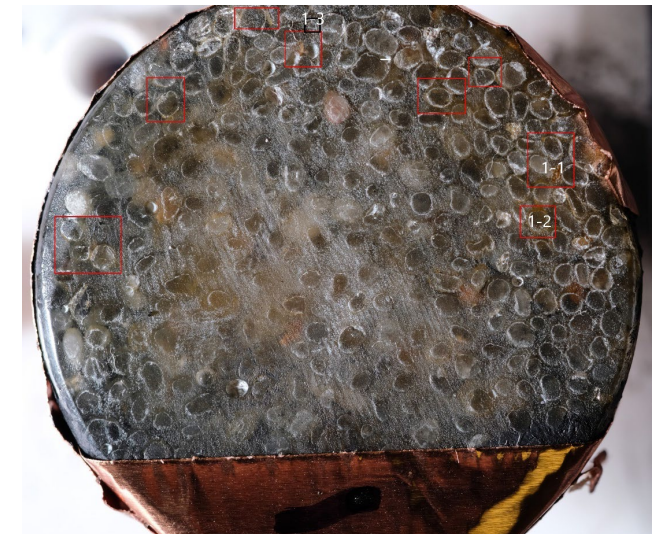
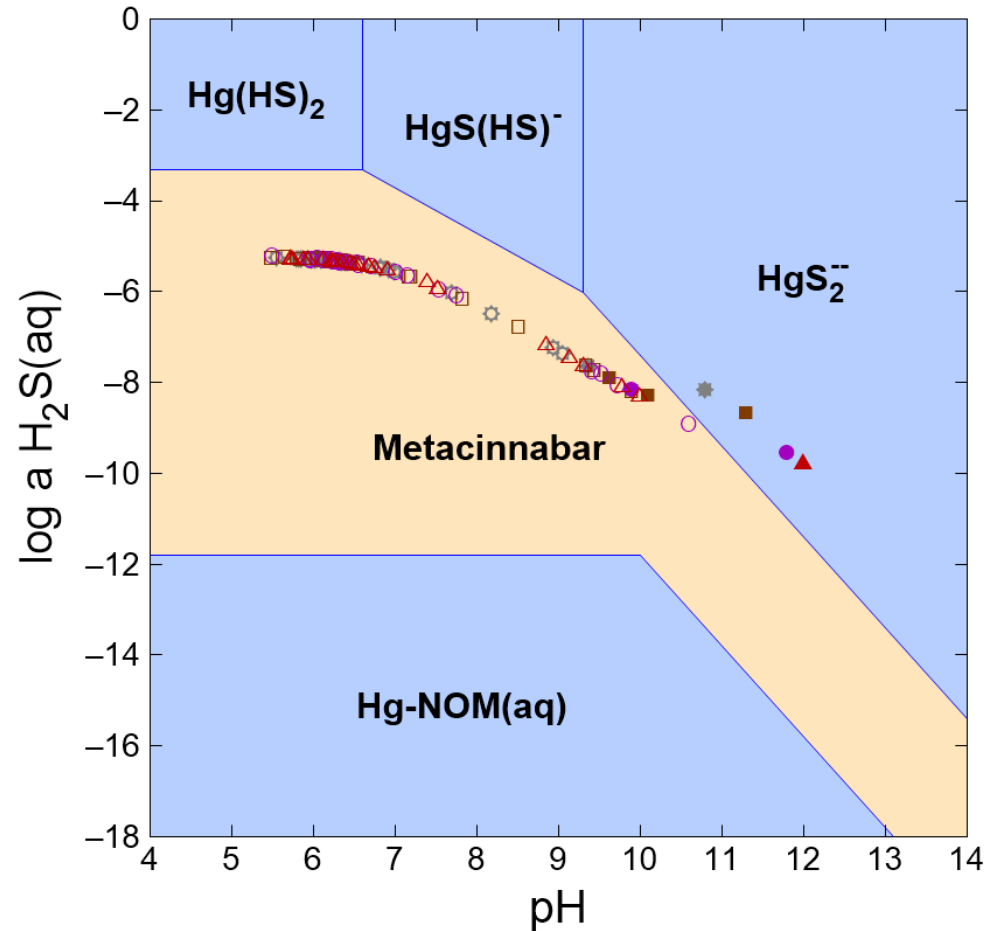
Four Years After Injection (2024)





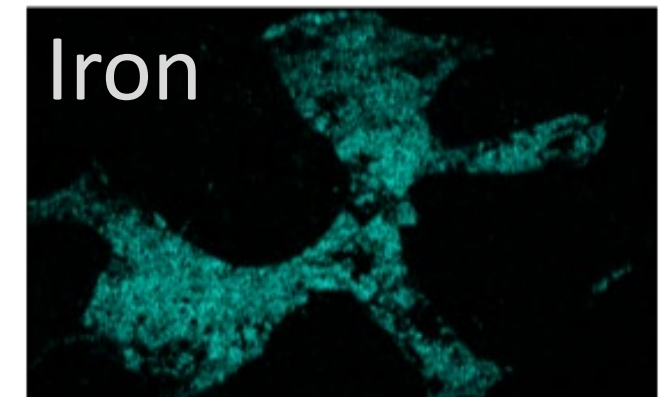
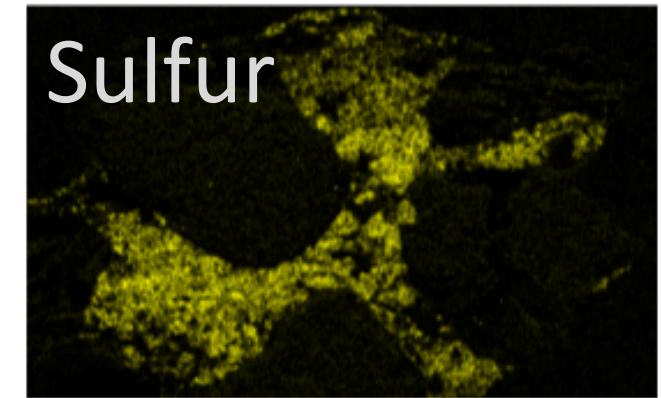
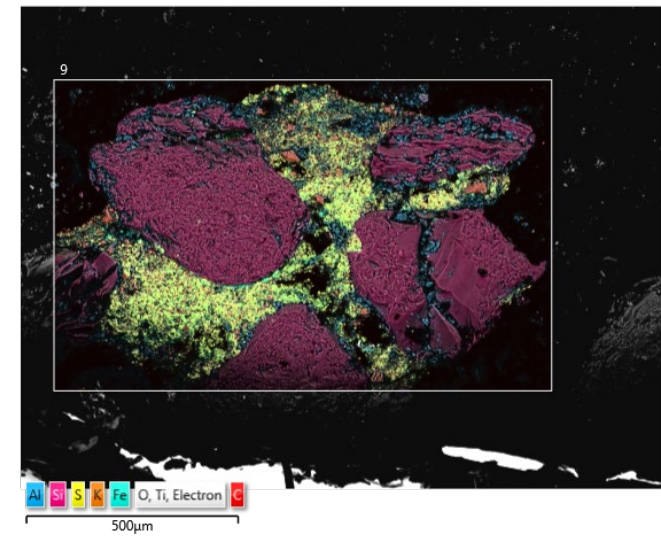
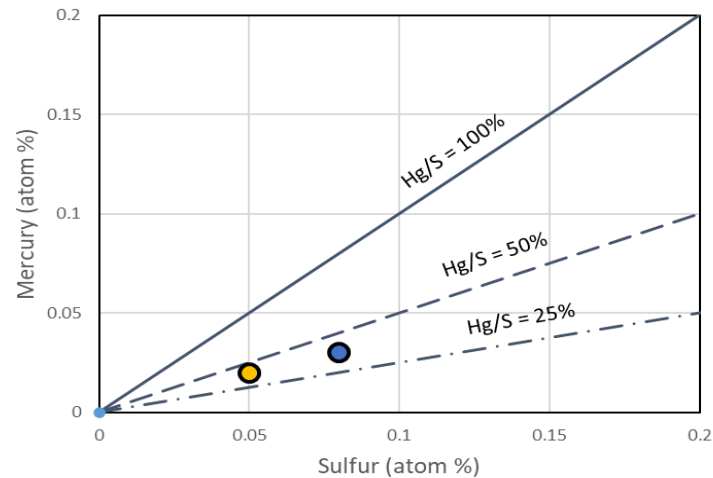
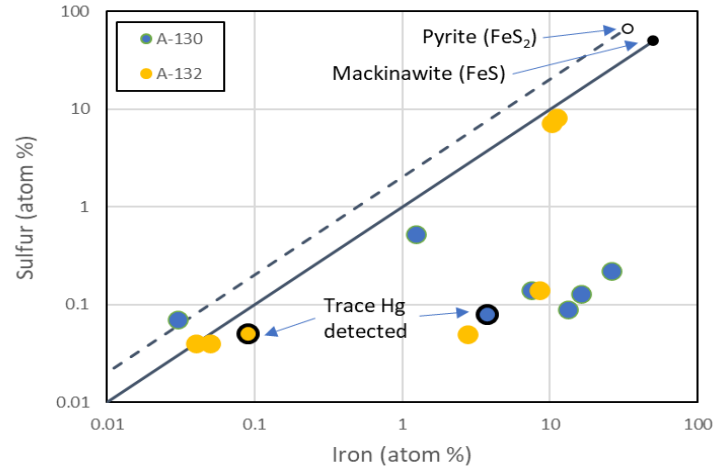
Treatment Stability Evaluation

- Geochemical conditions continue to be favorable for metacinnabar stability 4 years after injection
- Sand packets deployed to document Hg uptake by precipitates



Hg in Sulfide Precipitates

- Abundant, poorly crystalline iron sulfide (FeS) precipitates filled pore spaces between sand particles
- Mercury detected at trace levels confirming association with sulfide precipitates



Conclusions

- ISCF by sulfide precipitation demonstrated to be a viable technology for remediation of mercury in groundwater
 - Significant reduction of Hg plume concentrations and extent within months of injection
 - Ongoing treatment for several years following injection as reagent works its way through the system
 - Long-term treatment stability indicated by persistence of favorable geochemical conditions and confirmed by detection of Hg in neo-formed sulfide phases
- Accounting for reagent demand from Hg and non-target components is critical
- Injection design modeling key for reducing uncertainty in reagent dose and delivery (single versus multiple injections)